

**TITLE**

**COAL GASIFICATION WITH ALKALI ADDITIVES TO REDUCE EMISSIONS OF  
MERCURY TO THE ATMOSPHERE**

This Application claims priority from Provisional Patent Serial No. 60/441,005 filed January 17, 2003.

**BACKGROUND OF THE INVENTION**

**Field of the invention:**

[0001] This invention relates to a method for the reduction of mercury emissions from coal gasification processes. More particularly, it refers to an improved method for removal of mercury through the use of alkali additives in coal gasification and staged coal combustion processes.

**Description of the Prior Art:**

[0002] The 1990 Clean Air Act Amendments identified 189 substances that were designated as hazardous air pollutants (air toxins). These substances are chemicals, including heavy metals and organic compounds in both solid and gaseous forms, known to pose a risk to human health. One metallic element, mercury, is getting much attention due to its quantity and toxicity.

[0003] Mercury emissions to the air and releases to water occur naturally and by human activities. According to a fairly recent emissions inventory (1994-1995), in the United States the major emitters of mercury to the atmosphere were electric utilities, municipal waste combustors, commercial and industrial boilers, medical waste incinerators, and chlor-alkali plants. Until the middle of the decade, municipal waste combustors, hazardous waste combustors, and medical waste incinerators were the leading emitting source category. The United States Environmental Protection Agency (hereinafter

"EPA") now regulates these industries, and the EPA estimates that emissions from municipal waste combustors and medical waste incinerators declined by 90% from 1990 to 2000. This currently makes coal-fired utilities the leading man-made source of air-borne mercury emissions in the U.S. Of the estimated 5,000 tons of global mercury emissions emitted to the atmosphere in 1994-95, U.S. coal-fired power plants contributed about 51 tons, or 1%. This rate of mercury emissions represented 33% of the 158 tons of mercury released in the U.S. for the same time period.

[0004] There are several methods for removing elemental mercury and its compounds from combustion/incineration flue gas. Elemental mercury removal is somewhat difficult because mercury remains in the vapor phase at very low temperatures (boiling point at 674°F) and does not condense on ash particles in the flue gas stream so that it may be removed with electrostatic precipitators. However, removal of mercury from combustion flue gas (U.S. Patent No. 4,889,698 and U.S. Patent 5,672,323)) using activated carbon adsorption is known in the prior art. There are also other methods of removal; they include the use of oxidizing agents that convert elemental mercury to its soluble compound forms (U.S. Patent No. 5,900,042) so that it may be scrubbed from the flue gas. Another method, U.S. patent No. 6,214,304, uses alkali sulfides to convert elemental mercury to mercury sulfide that is removed by particulate control devices. Another method uses alkali injection into the boiler furnace (U.S. Patent No. 6,372,187); it has been shown to be somewhat effective in reducing mercury emissions. However, these methods, if highly effective (90% removal) like carbon adsorption are very expensive techniques (as high as \$100,000/lb of removal). The oxidizing method (U.S. Patent No. 5,900,042) and the alkali furnace injection method (U.S. 6,372,187) although less expensive, only remove 50 to 55% of the mercury.

[0005] It would therefore be advantageous to have an improved mercury capture technique that will reduce coal mercury emissions to the atmosphere and do so at a relatively low cost. The method of the present invention is inexpensive and is as effective if not more effective than the carbon adsorption method.

### **SUMMARY OF THE INVENTION**

[0006] I have discovered a process employing a staged combustor to remove mercury in an alkaline molten slag. High levels of mercury capture were found to be an inherent feature of a staged combustor (see U. S. Patent Nos. 4,395,975, 4,423,702 and 5,458,659) developed for the reduction of sulfur and nitrogen oxides to the atmosphere. Alkali compounds, such as limestone, lime, hydrated lime, dolomite, trona, nacholite or combinations thereof are added with the coal being fired in the first stage of the combustor, or are added separately into the first stage of combustion operating at 2400 to 2700°F. The first stage of combustion, in effect, is a coal gasifier operating at an air to fuel stoichiometric ratio of around 0.60. Sulfur and high levels of mercury capture are achieved through capture in the alkaline molten slag produced from the partial oxidation of any carbonaceous fuel, including coal, by incorporating a combustor design that yields a reducing condition in the alkaline molten slag sulfur capture zone. Nitrogen oxide emissions are also reduced by firing the coal in a substoichiometric air condition in the first stage that reduces NO<sub>x</sub> production from the oxidation of fuel bound nitrogen.

## **BRIEF DESCRIPTION OF THE DRAWINGS**

[0007] A more complete understanding of the invention can be obtained by considering the following detailed description in conjunction with the accompanying drawings, wherein;

[0008] Fig. 1 shows a schematic of a staged combustion system applied to a coal-fired boiler; and

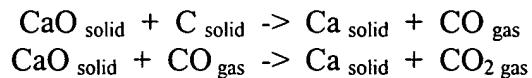
[0009] Fig. 2 shows the thermo chemical equilibrium for calcium and magnesium oxide reactions with carbon to form elemental calcium and magnesium.

## **DESCRIPTION OF THE PREFERRED EMBODIMENTS**

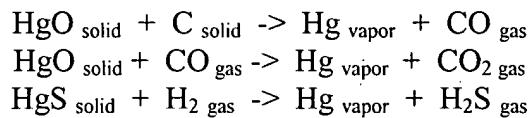
[0010] It is believed that the reaction mechanism for mercury capture in a molten slag bath gasifier involves the formation and capture of amalgams in complex mineral composites. Mercury will form amalgams with many alkali metals, alkaline earth metals, zinc, cadmium (Ca), arsenic, antimony, gold, silver and copper. Other metals like molybdenum, manganese, cobalt and particularly iron are nearly insoluble in mercury. It is believed that the high melting point alkaline earth metals Ca (melting point of 2192°F) and Magnesium (Mg) (melting point of 2030°F) that are combined with their oxide forms CaO (melting point of 4658°F) and MgO (melting point of 5072°F) are the alkaline earth metals that are forming amalgams with mercury. Under reducing conditions with carbon as the reducing agent for a gasifier temperature range of 2400 to 2700°F, both elemental calcium and magnesium can form; see the thermo chemical equilibrium coefficients for these reactions in Fig. 2. Although the equilibrium coefficients are low, still there would be orders of magnitude more concentration of elemental calcium and magnesium to react with all of the mercury in the coal. Since the coal is fired into the alkaline molten slag bath with enough force to swirl the slag, there should be plenty of carbon formed to create some quantity of elemental calcium and magnesium.

Carbon monoxide will also react with the oxides of calcium and magnesium to form elemental calcium and magnesium but the reactions are not quite as favored as the reactions with carbon.

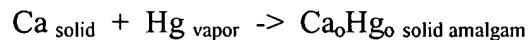
[0011] To achieve high mercury capture, the combustor is designed to provide for 1) intimate mixing of the carbonaceous fuel and its reactants with the reduced alkaline molten slag, and 2) intimate fuel/air mixing, done in such a way as to eliminate the formation of localized pockets of unreacted oxygen. By keeping the molten slag in a hot reducing condition (2200 to 2700°F), carbon and carbon monoxide react with certain metals to convert a portion of those metals to their elemental form that will then combine with mercury to form an amalgam; for example:



[0012] Mercury (Hg) is easily converted from its oxide and sulfide (Cinnabar) forms to elemental mercury:



[0013] For example, the elemental calcium then will react with elemental mercury to produce an amalgam that is tied up in a complex mineral composite.



[0014] The conclusion that amalgam formation is probably the cause of the nearly quantitative capture of mercury in the alkaline molten slag comes from the work done by Sir Humphrey Davy. In the early 1800's, Davy attempted to decompose a mixture of lime and mercuric oxide by an electric current and an amalgam of calcium was obtained. The separation of the mercury from the calcium

was then so difficult that Davy was not sure if he had obtained pure metallic calcium. Electrolysis of lime and calcium chloride in contact with mercury gave the same results.

[0015] Laboratory analysis for a three-stage combustor demonstration, wherein the first stage was operating at an air to fuel stoichiometric ratio that ranged from 0.58 of 0.77, firing an Illinois #5 coal with 3.39 wt% sulfur and with limestone being added at a Ca/S ratio of 0.85, showed the following results, see Table 1.

Table 1. Mercury Capture

Material:	Rate, lb/hr	Hg, ppmw	Hg, lb/hr	Capture, %
<b>Input:</b>				
Coal	1669.7	0.089	0.00014860	
Limestone (as CaO/MgO)	96.5	0.030	0.00000289	
<b>Total</b>	<b>1766.2</b>		<b>0.00015149</b>	
<b>Output:</b>				
Slag	38.9	2.60	0.00010110	66.7
Fly Ash	156.5	0.26	0.00004069	26.9
<b>Total</b>	<b>195.4</b>		<b>0.00014179</b>	<b>93.6</b>

[0016] Although a stack test was not completed for mercury emissions from the staged combustion system, from the weight rates and analyses of the different streams, mercury capture in primarily the first stage (gasifier) molten slag exceeded 90%. Even more impressive is that when leaching procedure tests were completed on the first stage (gasifier) slag and the fly ash removed from the flue gas baghouse, there was no leaching of mercury. Both samples of leachate yielded 0.0000 mg/l of mercury.

[0017] Mercury analyses were also completed on the ash from a coal-fired chain grate stoker at the same facility, firing the same Illinois #5 coal. The mercury in the fly ash was 0.079 ppmw and the

mercury in the grate bottom ash was 0.01 ppmw. This shows that mercury capture using a stoker is very low compared to the staged combustion system. This also indicates that for mercury capture to occur, a reducing condition must exist and limestone or some other alkali must be added. Data taken from a slagging cyclone boiler operation, firing Illinois coal wherein alkalis were not added that was operating under an overall oxidizing condition showed that about 8% of the mercury was captured in the bottom slag.

[0018] A typical example of the process of the present invention, preferably using the CAIRE™ staged combustor (U.S. Patent Nos. 4,423,702 and 5,458,659), is shown schematically in FIG. 1. Certain variations from this schematic could be made with such variations still being within the context of this invention. It will be understood by those skilled in the art that certain variations from this schematic could be made with such variations still being within the context of the present invention. In the embodiment shown in FIG. 1, a first stage combustor 10 is located in front of the entries 12 into the furnace 13. Openings 5 into each of the combustors receive a conventional fuel such as pulverized coal 2, and an alkaline product such as lime or limestone 3 with the carrier primary air 1 and the preheated air or oxygen 4. Alternatively, a coal water slurry pump could be used to convey pulverized coal to the combustor. Controlled partial oxidation of the coal takes place in the combustor by regulation of the preheated (400° to 700°F) secondary air or oxygen flow 4. The air (oxygen) to fuel stoichiometric ratio (SR) in first stage combustor 10 is maintained at about 0.40 to 0.70 ( $SR_1$ ) through control of the preheated air or oxygen flow 4, and most for air preferably at about 0.60. With the first stage combustor 10, the products of partial combustion in the form of a fuel gas and the molten slag from the ash portion of the coal plus the inorganic alkali compounds are separated in the first stage partial oxidation chamber 10, and a molten slag eutectic 7 containing

alkali compounds and coal ash exit through the bottom opening 8 of the first stage combustor 10.

The molten slag is quenched in a water quench sluice system 9 and the ash is sluiced to a collection tank from where it is pumped to a settling pond, or otherwise disposed of according to conventional known methods.

[0019] The staged combustor 10 has a partial oxidation zone where mixing at a temperature of about 2200° to 3000°F provides intimate contact between the coal and air or oxygen. Through the use of a staged combustor 10 that has incorporated molten slag removal, a high percentage (75-90%) of the molten slag produced during partial oxidation of the coal is removed from the gas prior to entry into the furnace 14, and prior to further partial oxidation at entry 12.

[0020] Although certain embodiments of the invention have been described in detail, it will be appreciated by those skilled in the art that various modifications and alterations would be developed in light of the overall teaching of the disclosure. Accordingly, the particular embodiments and arrangements disclosed herein are intended to be illustrative only and not limiting as to the scope of the invention which should be awarded the full breadth of the following claims and in any and all equivalents thereof.